

**DETERGENT COMPOSITIONS WITH  
PERFUME COMPLEXES TO MASK MALODORS**

**TECHNICAL FIELD**

The present invention relates to detergent and cleaning compositions, particularly liquid or gel dishwashing compositions suitable for use in manual dishwashing operations. These detergent compositions contain anionic surfactants, solvents and perfume/complexes, preferably perfume/cyclodextrin complexes, which are effective at covering malodors, particularly those malodors generated by nitrogenous compounds like amines. These components, in the combinations disclosed herein, are particularly effective in dishwashing detergent compositions which have preferred food soil cleaning, handling and sudsing characteristics without the odors typically associated with amines. The present invention also relates to the perfume compositions themselves and methods for masking malodors.

**BACKGROUND OF THE INVENTION**

Light-duty liquid (LDL) or gel detergent compositions useful for manual dishwashing are well known in the art. Such products are generally formulated to provide a number of widely diverse performance and aesthetics properties and characteristics. First and foremost, liquid or gel dishwashing products must be formulated with types and amounts of surfactants and other cleaning adjuvants that will provide acceptable solubilization and removal of food soils, especially greasy soils, from dishware being cleaned with, or in aqueous solutions formed from such products. Thus, there is a continuing effort by formulators of liquid dishwashing compositions to incorporate additional components into LDL detergents to provide consumers with improved cleaning benefits.

Diamines are a type of nitrogenous compound which can improve the cleaning performance of liquid dishwashing detergent compositions, in particular the cleaning of greasy, hydrophobic soils on dishware or other kitchen articles. However, diamines can also cause extremely potent malodors, such as the unpleasant fragrance associated with permanent kits commonly used to curl hair.

Also, nitrogen-containing surfactants and polymers can provide both cleaning and sudsing advantages, but frequently contain amine impurities as by-products in commercial materials. When the composition approaches or exceeds the pKa of these amine impurities, the resultant free amine can be malodorous. Consequently, it has been difficult to formulate a malodor-free light duty liquid at pH higher than about 8.5.

Typically malodors associated with liquid dishwashing detergents are “masked” (covered up) by placing a perfume composition in the liquid dishwashing detergent, which when used in sufficient quantities, would mask the malodor emanating from the liquid detergent. These perfumes also provided the added benefit that a desirable fragrance, such as a lemon scent, could be imparted to the liquid detergent product.

However, in recent years it has become desirable to use liquid dishwashing detergent formulations that have a higher product concentration, i.e., compact formulations. The prime advantages of compact formulations is that they require less storage space and deliver more value to the consumer. Because lower amounts of compact formulations are dosed into the wash solution during the wash process, it is necessary to increase the perfume concentration in the compact formulation to insure that a sufficient amount of malodor-suppressing perfume compositions are present during the wash process. But these high levels of perfume in a detergent composition can be difficult to stabilize and may give the liquid dishwashing detergent composition an intensely strong “perfumed” odor that many consumers dislike.

Given the foregoing there is a continuing need to formulate liquid dishwashing detergent compositions, particularly in compact formulations, that provide excellent cleaning benefits, but do not have malodors associated with them or their use during a manual dishwashing process. Accordingly a benefit of the present invention is that a liquid dishwashing detergent is prepared which provides excellent cleaning performance during a manual dishwashing process but is effective at suppressing the malodors released during the wash process. An additional benefit of the present invention is that such malodors are suppressed without providing the detergent composition an intensely-strong perfume odor but while at the same time emanating an acceptable scent during the wash process.

A further, additional benefit of the present invention is that it offers a way of imparting two distinct and different fragrant scents to a consumer product. This could be a useful way to convey to a consumer, via an olfactory signal, that a detergent product has two distinct benefits, for example that it is both tough on grease, while at the same time is gentle and mild to the skin.

The benefits of this invention can be included in containers for a broad variety of liquid detergent products. Such products may include LDLs, liquid hand soap, shampoo, after shave, cologne and personal deodorants, other personal care compositions, hard surface cleaners and a variety of other home and personal care products in which odor-emanating compounds like amines may be present and it is desirable to mask any malodors that they may generate.

#### **SUMMARY OF THE INVENTION**

It has now been determined that a liquid detergent composition can be prepared which provides excellent cleaning performance and which is particularly effective at masking the malodors generated during use of the liquid detergent (such as in a manual dish washing process) by the incorporation of perfumes as well as perfume delivery and odor-suppression technology.

Specifically, the perfume delivery technology and odor-suppression technology relates to complexing agents having an internal cavity and are capable of forming complexes with the fragrance material ingredients of the perfume compositions. By forming such complexes, the fragrance material ingredients are maintained in the liquid detergent until they are released during a manual wash process.

In a preferred embodiment of the present invention relates to a liquid detergent composition which comprises an anionic surfactant, a solvent and fragrance materials; wherein a portion of the fragrance materials are complexed with water-soluble cyclodextrin molecules while another portion are uncomplexed.

The present invention also comprises a process for forming an aqueous liquid detergent composition comprising a first step of forming a complexing mixture of fragrance materials, water-soluble cyclodextrin molecules and propylene glycol and in a second step adding the complexing mixture to a solution comprising an anionic surfactant and a solvent.

All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

### **DETAILED DESCRIPTION OF THE INVENTION**

**Definitions** - The present detergent compositions comprise an "effective amount" or a "grease removal-improving amount" of individual components defined herein. By an "effective amount" of the diamines herein and adjunct ingredients herein is meant an amount which is sufficient to improve, either directionally or significantly at the 90% confidence level, the performance of the cleaning composition against at least some of the target soils and stains. Thus, in a composition whose targets include certain grease stains, the formulator will use sufficient diamine to at least directionally improve cleaning performance against such stains.

By "light-duty liquid (LDL) detergent composition" it is meant a detergent composition which is employed in manual (i.e. hand) dishwashing.

By "kitchen articles" it is meant cookware, flatware, dishes and dishware, silverware and other articles commonly found in the kitchen and used for the preparation, consumption and serving of food as well as those articles used for cleaning up at the conclusion of a meal or other food preparation.

By "nitrogenous compounds" it is meant those compounds containing nitrogen and related to ammonia or ammonium. Such compounds include amines, polyamines, amine oxide surfactants, amides, surfactants in which the hydrophilic, polar groups are neutralized by an ammonium cation, alkanolamine solvents (e.g. monoethanolamine, diethanolamine, and triethanolamine) and other similar compounds which are typically used in detergent or cleaning compositions.

By "malodor" it is meant any detectable odor associated with and originating in any component of a detergent composition with the exception of fragrance materials; particularly short-chain fatty acids or an amine or other nitrogenous compound related to ammonia or ammonium.

By "amine" it is meant any derivative of ammonia or ammonium in which one or more of the hydrogen atoms is replaced by an alkyl group, a cyclic hydrocarbon group, a fatty alkyl group or an aromatic group.

By "scent" it is meant any detectable odor associated with and originating in a fragrance material.

By "volatility" it is meant the tendency of a liquid material to pass into the vapor state at a given temperature.

The present invention is directed to detergent and cleaning compositions, particularly liquid dishwashing detergent compositions, which include perfume compositions and complexing agents having an internal cavity and are capable of forming complexes with ingredients of the perfume compositions; such complexing agents include molecules such as zeolites, callixaranes and cyclodextrins with a cavity size of from about 50 Å to about 300 Å, preferably from about 65 Å to about 210 Å. In a preferred embodiment, the complexing agents are cyclodextrins. In this preferred embodiment, the cyclodextrin and perfume compositions are particularly effective at masking the malodors generated by a broad array of malodors, but particularly those malodors generated by nitrogenous compounds such as amines. These nitrogenous compounds can be added either intentionally to provide some performance benefit for the detergent or cleaning composition or may be introduced inadvertently as impurities in the surfactant additives (particularly in amine oxide, betaine and polyhydroxy fatty acid amide surfactants) and in amine-containing polymers.

#### Cyclodextrin/Perfume Fragrance Complexes and Free Perfume Compositions

An essential aspect of the present invention is that the liquid detergent compositions taught herein contain complexes of cyclodextrin and fragrance materials. As discussed below, fragrance materials are the ingredients which form a perfume composition. The present detergent

compositions will also contain free fragrance materials which when brought into the presence of cyclodextrin molecules are not incorporated into the molecule's cavity and remain as free molecules.

(a) Cyclodextrin Molecules — Cyclodextrin molecules are known for their ability to form complexes with perfume ingredients and have typically been taught as a perfume carrier. In addition, cyclodextrin molecules also appear to be surprisingly effective at reducing malodors generated by nitrogenous compounds, such as amines.

The prior art teaches the use of drier-added fabric softener sheets containing high levels of cyclodextrin/perfume complexes wherein the fabrics treated with this solid cyclodextrin complex release perfume when the fabrics are rewetted and that these cyclodextrin/perfume complexes can be used in aqueous rinse-added fabric softener compositions without being protected. By "protected" it is meant that the cyclodextrin is encapsulated in a hydrophobic wax coating so the cyclodextrin/perfume complexes will not decompose due to the presence of water. See e.g. U.S. Pat. No. 5,578,563, issued Nov. 26, 1996, to Trinh et al., which is hereby incorporated by reference. Thus the cyclodextrin used in the present invention may either be "unprotected", as discussed above, or "protected" by the hydrophobic-coating protection techniques discussed in the prior art; see e.g. U.S. Pat. No. 5,102,564 to Gardlik et al., issued Apr. 7, 1992; U.S. Pat. No. 5,234,610, to Gardlik et al., issued Aug. 10, 1993.

The cavity of a cyclodextrin molecule has a substantially conical shape. It is preferable in the present invention that the cone-shaped cavity of the cyclodextrins have a length (altitude) of about 8 Å and a base size of from about 5 Å to about 8.5 Å. Thus the preferred cavity volume for cyclodextrins of the present invention is from about 65 Å<sup>3</sup> to about 210 Å<sup>3</sup>.

Suitable cyclodextrin species include any of the known cyclodextrins such as unsubstituted cyclodextrins containing from six to twelve glucose units, especially, alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin and/or their derivatives and/or mixtures thereof. The alpha-cyclodextrin consists of six glucose units, the beta-cyclodextrin consists of seven glucose units, and the gamma-cyclodextrin consists of eight glucose units arranged in a donut-shaped ring. The specific coupling and conformation of the glucose units give the cyclodextrins a rigid, conical molecular structure with a hollow interior of a specific volume. The "lining" of the internal cavity is formed by hydrogen atoms and glycosidic bridging oxygen atoms, therefore this surface is fairly hydrophobic. The unique shape and physical-chemical property of the cavity enable the cyclodextrin molecules to absorb (form inclusion complexes

with) organic molecules or parts of organic molecules which can fit into the cavity. Many perfume molecules can fit into the cavity.

It is an essential element of the present invention that the cyclodextrin molecules be water-soluble. The water-soluble cyclodextrins used herein preferably have a water solubility of at least about 10 g in 100 ml water, more preferably at least about 25 g in 100 ml of water at standard temperature and pressure. Examples of preferred water-soluble cyclodextrin derivative species suitable for use herein are hydroxypropyl alpha-cyclodextrin, methylareal alpha-cyclodextrin, methylated beta-cyclodextrin, hydroxyethyl beta-cyclodextrin, and hydroxypropyl beta-cyclodextrin. Hydroxyalkyl cyclodextrin derivatives preferably have a degree of substitution of from about 1 to about 14, more preferably from about 1.5 to about 7, wherein the total number of OR groups per cyclodextrin is defined as the degree of substitution. Methylated cyclodextrin derivatives typically have a degree of substitution of from about 1 to about 18, preferably from about 3 to about 16. A known methylated beta-cyclodextrin is heptakis-2,6-di-O-methyl-beta-cyclodextrin, commonly known as DIMEB, in which each glucose unit has about 2 methyl groups with a degree of substitution of about 14. A preferred, more commercially available methylated beta-cyclodextrin is a randomly methylated beta-cyclodextrin having a degree of substitution of about 12.6. The preferred cyclodextrins are available, e.g., from American Maize-Products Company and Wacker Chemicals (USA), Inc.

Further cyclodextrin species suitable for use in the present invention include and include alpha-cyclodextrin and derivatives thereof, gamma-cyclodextrin and derivatives thereof, derivatised beta-cyclodextrins, and/or mixtures thereof. Other derivatives of cyclodextrin which are suitable for use in the present invention are discussed in U.S. Pat. No. 5,578,563, incorporated above.

It should be noted that two or more different species of cyclodextrin may be used in the same liquid detergent composition.

#### b) Formation of Complexes

The complexes of this invention are formed in any of the ways known in the art. Typically, the complexes are formed either by bringing the fragrance materials and the cyclodextrin together in a suitable solvent (propylene glycol is preferred). Additional examples of suitable processes as well as further preferred processing parameters and conditions are disclosed in U.S. Pat. No. 5,234,610, to Gardlik et al., issued August 10, 1993, which is hereby incorporated by reference. After the cyclodextrin and fragrance materials are mixed together, this mixture is added to the liquid detergent composition.

Generally, only a portion (not all) of the fragrance materials mixed with the cyclodextrin will be encapsulated by the cyclodextrin and form part of the cyclodextrin/perfume complex; the remaining fragrance materials will be free of the cyclodextrin and when the cyclodextrin/perfume mixture is added to the detergent composition they will enter the detergent composition as free perfume molecules. A portion of free cyclodextrin molecules which are not complexed with the fragrance materials may also be present.

In an alternative embodiment of the present invention, the fragrance materials and cyclodextrins are added uncomplexed and separately to the liquid detergent compositions. Consequently, the cyclodextrins and fragrance materials will come into the presence of each other in the composition, and a portion of each will combine to form the desired fragrance materials/cyclodextrin complex.

Suitable fragrance materials for use in the present invention are described in greater detail below.

In general, perfume/cyclodextrin complexes have a molar ratio of perfume compound to cyclodextrin of 1:1. However, the molar ratio can be either higher or lower, depending on the size of the perfume compound and the identity of the cyclodextrin compound. In the present invention the molar ratio of fragrance materials to cyclodextrin is preferably from about 4:1 to about 1:4, more preferably from about 1.5:1 to about 1:2, most preferably from about 1:1 to about 1:1.5. The molar ratio can be determined easily by forming a saturated solution of the cyclodextrin and adding the perfume to form the complex. In general the complex will precipitate readily. If not, the complex can usually be precipitated by the addition of electrolyte, change of pH, cooling, etc. The complex can then be analyzed to determine the ratio of perfume to cyclodextrin.

The actual complexes are determined by the size of the cavity in the cyclodextrin and the size of the perfume molecule. Although the normal complex is one molecule of perfume in one molecule of cyclodextrin, complexes can be formed between one molecule of perfume and two molecules of cyclodextrin when the perfume molecule is large and contains two portions that can fit in the cyclodextrin. Highly desirable complexes can be formed using mixtures of cyclodextrins since perfumes are normally mixtures of materials that vary widely in size. It is usually desirable that at least a majority of the material be beta- and/or gamma-cyclodextrin. It is highly desirable to use the reaction mixtures from the intermediate stages of the manufacture of the pure cyclodextrins as discussed hereinbefore.

#### c) Fragrance Materials and Odor Neutralizers

In the present invention, fragrance materials are complexed with cyclodextrin to form a cyclodextrin/perfume complex and optionally may also be added directly as to a detergent composition as part of a free perfume composition. As discussed below, the criteria for selecting fragrance materials for use in the present invention will be based on one or more of these three criteria: volatility, hydrophobicity and potency.

While not intending to be limited by theory it is believed that the ability of fragrance materials contained in the present perfume compositions to mask malodors is related both to: 1) the amount of time that the scents emanating from the fragrances require to diffuse into the air and hence move from the detergent composition containers to the nasal receptor sites; and 2) the relative potency of a scent or malodor.

The rate at which a fragrance material diffuses into the air and hence escapes the detergent composition can also be related to its hydrophobicity, which is discussed in more detail below.

Thus the fragrance materials which constitute the perfume compositions and from part of the perfume/cyclodextrin complex of the present invention will be selected based on one or more of these three criteria: volatility, hydrophobicity and potency. In addition, for the fragrance materials which are to form part of the perfume/cyclodextrin complex a fourth criteria must be added: size, because the fragrance material molecule must be of suitably small size (and hence of a suitably small molecular weight) so that it is capable of fitting within the internal cavity of a cyclodextrin molecule.

i) Volatility

The fragrance materials found in the present detergent compositions preferably contain volatile fragrance materials. These volatile fragrance materials have lower boiling points than other substances and so the scents from these materials quickly diffuse into the air, and compete with the malodors to bind to the nasal receptor sites. Becoming the first odors recognized and identified by the brain. Because the scents from these volatile fragrance materials are more volatile and arrive before the amine malodors at the nasal receptor sites, when the amine malodors do finally arrive the nasal receptor sites have already been occupied thus effectively masking the recognition of the amine malodors.

As used in this present invention, volatile fragrance materials have a boiling point of below about 250°C, more preferably below about 230°C, most preferably below about 210°C under 1 atmosphere of pressure.

Most low molecular weight aldehydes, ketones, and esters have relatively low boiling points and are thus examples of volatile fragrance materials suitable for use in the present



invention. Further nonlimiting examples of suitable highly volatile fragrance materials and their respective boiling point values under 1 atmosphere of pressure include the following:

<u>Fragrance Material</u>	<u>Boiling Point (°C)</u>
3,7-dimethyl-7-hydroxyoctan-1-al	241
methyl-2-aminobenzoate	237
2-cis-3,7-dimethyl-2,6-octadien-1-ol	227
n-decyl aldehyde	215
benzaldehyde	179
Methyl acetoacetate	172
Isopropyl 2-methylbutyrate	138
ethyl-2-methylbutyrate	131

The boiling point of many perfume materials are disclosed in, e.g., "Perfume and Flavor Chemicals (Aroma Chemicals)," S. Arctander, published by the author, 1969, incorporated herein by reference. Other boiling point values can be obtained from different chemistry handbooks and databases, such as the Beilstein Handbook, Lange's Handbook of Chemistry, and the CRC Handbook of Chemistry and Physics. When a boiling point is given only at a different pressure, usually lower pressure than the normal pressure of one atmosphere, the boiling point at normal or ambient pressure can be approximately estimated by using boiling point-pressure nomographs, such as those given in "The Chemist's Companion," A. J. Gordon and R. A. Ford, John Wiley & Sons Publishers, 1972, pp. 30-36. When applicable, the boiling point values can also be calculated by computer programs, based on molecular structural data, such as those described in "Computer-Assisted Prediction of Normal Boiling Points of Pyrans and Pyrroles," D. T. Stanton et al, J. Chem. Inf. Comput. Sci., 32 (1992), pp. 306-316, "Computer-Assisted Prediction of Normal Boiling Points of Furans, Tetrahydrofurans, and Thiophenes," D. T. Stanton et al, J. Chem. Inf. Comput. Sci., 31 (1992), pp. 301-310, and references cited therein, and "Predicting Physical Properties from Molecular Structure," R. Murugan et al, Chemtech, June 1994, pp. 17-23. All the above publications are incorporated herein by reference.

The detergent compositions of the present invention are more effective at masking malodors (such as those originating in nitrogenous compounds) when they include fragrance materials in a "layered" arrangement—i.e. the fragrance materials included have boiling points located at a variety of different temperatures. This works most effectively because, as summarized above, the present perfume compositions effectively mask the most volatile malodors because they

include fragrance materials with low boiling points and so the fragrance materials quickly diffuse into the air and arrive at the nasal receptor sites before the malodors, therefore effectively masking the malodors. However, it is possible that after sufficient time has passed and the malodors have arrived in the physical proximity of the nasal receptors sites, scents already resident in the sites may degrade or migrate out of them; thus giving the malodors an opportunity to bind with the sites and thereby making the odors perceptible to consumers. This is especially the case if there is a higher concentration of malodors or the malodors are more potent than the scents from highly volatile fragrance materials.

Thus to prevent this, it is preferable to include, in addition to the fragrance materials with a low boiling point, additional fragrance materials with somewhat higher boiling points. The scents from these fragrance materials should arrive either simultaneously or soon after the malodors and compete with the malodors for the sites vacated as scents emitted by the highly volatile fragrance materials degrade or migrate out of the nasal receptor sites.

Overall, the perfume compositions of the present invention may comprise from about 30 % to about 50 % , preferably from about 35 % to about 50 %, most preferably from about 40 % to about 45 %, of volatile fragrance materials.

ii) Hydrophobicity

Another important parameter of the fragrance materials used in the present invention is the degree of hydrophobicity. Liquid detergent compositions of the present invention may be heavily diluted, having formulas containing as much as 80 % of water. Thus while the product is being stored, hydrophobic fragrance materials are more likely to concentrate themselves at the interface between the liquid detergent composition and the headspace in the detergent container (e.g. squeeze bottle) air located in the bottle in which the liquid dishwashing detergent is contained. When the product is used by a consumer, those fragrance materials which are more hydrophobic will be positioned on the liquid detergent-air interface and thus more readily evaporate into the air to provide pleasant fragrant signaling.

The degree of hydrophobicity of a fragrance material can be correlated with its octanol/water partitioning coefficient ("P"). The octanol/water partitioning coefficient of a fragrance material is the ratio between its equilibrium concentration in octanol and in water. A fragrance material with a greater partitioning coefficient P is more hydrophobic. Conversely, a fragrance material with a smaller partitioning coefficient P is more hydrophilic. The preferred fragrance materials of the present invention have an octanol/water partitioning coefficient P of

1000 or greater. Since the partitioning coefficients of the fragrance materials normally have high value, they are more conveniently given in the form of their logarithm to the base 10,  $\log P$ .

The detergent compositions of the present invention will comprise from about 0.01% to about 10% of fragrance materials having a  $\text{ClogP} \leq 3$ , preferably from about 0.05% to about 5% of fragrance materials having a  $\text{ClogP}$  value of  $\leq 3$ ; more preferably from about 0.075% to about 1% of fragrance materials having a  $\text{ClogP}$  value of  $\leq 3$ .

The  $\log P$  of many perfume ingredients has been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylog CIS), Irvine, Calif., contains many, along with citations to the original literature. However, the  $\log P$  values are most conveniently calculated by the "CLOGP" program, also available from Daylight CIS. This program also lists experimental  $\log P$  values when they are available in the Pomona92 database. The "calculated  $\log P$ " ( $\text{ClogP}$ ) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990, incorporated herein by reference). The fragment approach is based on the chemical structure of each perfume ingredient, and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. The  $\text{ClogP}$  values, which are the most reliable and widely used estimates for this physicochemical property, are used instead of the experimental  $\log P$  values in the selection of perfume ingredients which are useful in the present invention.

Because it is more likely that the more hydrophobic materials will be encapsulated in the cyclodextrin molecules in an optional aspect of the present invention the fragrance materials are selected such that up to about 75% of the fragrance materials in the cyclodextrin complex will have a  $\text{ClogP}$  of  $\geq 3$  while up to about 75% of the uncomplexed fragrance materials will have a  $\text{ClogP}$  of  $\leq 3$ .

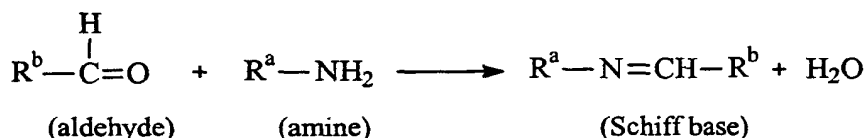
Nonlimiting examples of suitable fragrance materials and their respective  $\text{ClogP}$  values include the following:

<u>Perfume Material</u>	<u>ClogP</u>
para-Ethyl-alpha, alpha-dimethylHydro-cinnamaldehyde	3.4
Isobutyl caproate	3.8
4-tert.-butylcyclohexyl acetate	4.1

(iv) Size/molecular weight – As discussed above, when selecting fragrance materials to include in a cyclodextrin/perfume complex, it is necessary to insure that the fragrance material molecule must be of suitably small size (and hence of a suitably small molecular weight) so that it is capable of fitting within the internal cavity of a cyclodextrin molecule—although a perfume molecule may be larger than the internal cavity of an individual cyclodextrin molecule, provided that parts of the perfume molecule may be contained in two or more cyclodextrin molecules.

(v) Odor Neutralizers – A particular type of fragrance material is an odor neutralizer.

Odor neutralizers are like fragrance materials in that they emit a scent, but they also mask the malodors by reducing the amount of the amines generating the malodor. Any chemical species that upon reacting with an amine yields products which generate little or significantly less malodor than amines is suitable as an odor neutralizer. A preferred species of odor neutralizers are aldehydes; it is well known that aldehydes react with amines in a Schiff reaction to produce a Schiff base and water:



In the above reaction, R<sup>a</sup> and R<sup>b</sup> are both aliphatic substituents. In the present invention the amine may be a diamine included for the benefits it provides on tenacious, hydrophobic and greasy soils. See the discussion of diamines below.

Schiff bases generate little or no malodor and thus by reacting an aldehyde with an amine they reduce the amount of the amine which is present to generate malodors. Aldehyde classes suitable for use in the present invention include Muguet, Citrus, Ozone, Aquatic and Green Aldehydes. Particularly desirable aldehyde fragrance materials of these classes are as follows:

Muguet Aldehydes: P.T. Bucinal (lilial), Hydroxycitronellal, Lylal (3-cyclohexene-1-carboxy-aldehyde, 4-(4-hydroxy-4-methyl pentyl).

Citrus Aldehydes: Octyl aldehyde (caprylic aldehyde), Nonyl aldehyde (Pelargonic aldehyde), Decyl aldehyde (capric aldehyde), Methyl nonyl acetaldehyde, Methyl octyl acetaldehyde, Undecylic aldehyde (n-undecanal), Citronellal, Myrac aldehyde (iso hexenyl tetrahydro benzaldehyde).

Ozone Aldehydes, Aquatic Aldehyde and Green Aldehydes: XI aldehyde (acetaldehyde, para-methyl phenoxy) Melonal Canthoxal (2-methyl-3-(para-methoxy phenyl)-propanal) Floralozone (para-ethyl-alpha, alpha-dimethyl hydrocinnamaldehyde) Geraldehyde (5,9-dimethyl-4,8-decadienal) Helional ( hydrocinnamaldehyde, alpha-methyl-3,4-methylenedioxy), Triplal (3-cyclohexene-1-carboxaldehyde,2,4-dimethyl) Melozone (4,7-methanoindan-1-carboxaldehyde), Ligustral

These fragrance materials in addition providing odor neutralizing benefits also emit a characteristic scent and thus serve in the present invention as a fragrance material.

d) Distribution of Fragrance Materials in Complex and in Detergent Composition

The liquid detergent compositions of the present invention contain complexes of cyclodextrin and fragrance materials. Because the cyclodextrin encapsulates these fragrance materials, the cyclodextrin/perfume complex does not significantly affect the liquid detergent composition's odor during storage, non-use and at the initial dispensing at the beginning of use. (Note, however, that when the cyclodextrin-fragrance material mixture is initially added to the detergent composition during manufacture this mixture may alter the liquid detergent composition's odor because the mixture contains amount of free fragrance materials which are not complexed with the cyclodextrin.)

When the detergent composition is used (e.g. during a manual dishwashing operation) the fragrance materials in the complex are released to deliver a perfume "bloom" detectable by the consumer and different from the odor sensed during storage and initial dispensing. Such released may be caused by a variety of factors experienced during use of the complex-containing liquid detergent such as: increased temperature, mechanical agitation or change in the electrolyte concentration.

In a preferred embodiment, in addition to those fragrance materials found in the cyclodextrin/perfume complex, a free perfume composition containing certain fragrance materials may also be added directly to the liquid detergent composition. Thus by including one set of fragrance materials in the cyclodextrin complex and another set of fragrance materials in a perfume composition which is added directly to the liquid detergent product it is possible to provide both an initial odor and a delayed odor. The initial odor is the odor perceived by the consumer when the consumer first exposes the product to air (e.g. by removing the lid or placing

a portion of the detergent composition on a sponge) while the delayed odor is the odor perceived by the consumer during of the liquid detergent composition (e.g. in a manual dishwashing operation). The initial odor is supplied by the free perfume composition in the liquid detergent (as well as the malodors therein as well) while the delayed odor is supplied by fragrance materials encapsulated by the cyclodextrins and released during use.

The use of an initial and a delayed odor offers a way of imparting two distinct and different fragrant scents to a consumer product. For example the initial odor conveys that it is tough on grease while the delayed odor indicates the composition is gentle and mild to the skin.

e) Fragrance Material Endurance Test

The compositions of the present invention are particularly suitable for imparting a pleasant and enduring fragrance scent to the consumer product. These fragrance scents are particularly beneficial because they may impart to the consumer's environment and enduring and linger pleasant odor. The ability of these compositions to impart an enduring fragrance to the consumer environment may be measured by means of headspace analysis index.

The following illustrates a step-by-step procedure for determining the index of fragrance material endurance and the index of selective fragrance material endurance making use of a simulation chamber designed to mimic the dishwashing habit:

1. 70 ml of tap water was adjusted to a  $\text{CaCO}_3$  concentration of 7 mg/L by combining with deionized-distilled water. This amount of tap water was then added into a sampling chamber and allowed to stir for four hours.  
0.18 g of a LDL liquid detergent composition was then added to the stirring water and Helium purged at a flow rate of 20 mL/min.
2. a headspace collection was made on a pre-made trap containing Tenax TA packing and run via gas chromatography/mass spectroscopy/low velocity intense source. The collection was made for 5 minutes. Separate collections were taken at 2 min, 30 min, 60 min, 2 hr, 4 hr, 24 hr, 48 hr, 72 hr. Flow and solution temperature was monitored during sampling . (Room temperature samples were performed on the bench-top, the elevated temperature was achieved by placing entire sampling unit in an oven.)
3. Integrated peak area counts from flame ionization detection response were calculated for relative comparison.

The concentration of fragrance materials as measured using the peak area count is preferably at least  $9 \times 10^6$  after 24 hours. More preferably the peak area count is preferably at least  $15 \times 10^6$  after 24 hours, even more preferably at least  $5 \times 10^6$  after 48 hours and most preferably at least  $5 \times 10^6$  after 72 hours,

#### DETERGENT COMPOSITIONS

The cyclodextrin technology discussed above may be used in several different types of liquid detergent compositions such as LDLs, liquid or gel automatic washing machine detergents, liquid hand soap, shampoo, after shave, cologne and personal deodorants, other personal care compositions, hard surface cleaners and a variety of other home and personal care products in which odor-emanating compounds like amines may be present and it is desirable to mask any malodors that they may generate. Thus many different types of liquid detergent compositions contain active ingredients which are also malodor-generating compounds. For example, a malodor-generating compound which is used in shampoos is a cationic polymer comprising nitrogenous monomeric units such as dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate etc. See, e.g. U.S. Pat. No. 5,624,666, to Coffindaffer et al., issued April 29, 1997, which is hereby incorporated by reference.

Other malodor-generating compounds which can be useful in hair and skin-care products as well as other liquid detergents include polymers such as gums and resins which are primarily derived from natural sources; crosslinked nonionic polyacrylate polymers and crosslinked cationic polyacrylate polymers such as homopolymers, copolymers, terpolymers of quaternary ammonium or cationic amine-substituted monomer units; polysaccharide polymers such as those derived from cellulose and starch; protein polymers; carboxylic acid polymers such as crosslinked acrylic acid homopolymers or copolymers; substituted or unsubstituted, linear or branched polyacrylamide polymers; copolymers of alkyl vinyl ethers and maleic anhydride; polyvinyl (N-pyrrolidones); silicone polymer materials (excluding the volatile silicone derivatives useful as a malodor-producing liquid carrier described hereinbelow) such as polydimethylsiloxane gums, silicone elastomers, siloxane gums, resin reinforced siloxanes, and crosslinked siloxane polymers; as well as silicone copolymers useful as hair styling polymers; and mixtures thereof. U.S. Pat. No. 5,919,400, to Kasier et al., issued July 6, 1999, which is hereby incorporated by reference.

The malodor-generating amine-substituted groups mentioned above, e.g.

=N—C(=O)— monomer groups which provide dye-transfer inhibition benefits, can also be used in liquid fabric softener products. See, e.g. U.S. Pat. No. 5,804,219, to Trinh et al., issued September 8, 1998, which is hereby incorporated by reference.

Amide-based nonionic surfactants such as hydrocarbylamidoalkylenesulfobetaine, which are often used in liquid detergents such as countertop, glass and surface cleaners, can also be a potent source of malodors. See, e.g. U.S. Pat. No. 5,108,660, to Michael, issued April 28, 1992, which is hereby incorporated by reference.

These liquid detergent products and the malodor-generating compounds they contain which have been previously mentioned are discussed only as examples to be illustrative of the breadth and benefits of the present invention, but are not meant to limit the scope of the malodor-suppression technology to the malodor-generating compounds or the liquid detergent products which have been specifically mentioned.

#### Liquid Dishwashing Compositions

In addition to the types of liquid detergents discussed above, the cyclodextrin technology is particularly useful for inclusion in a liquid dishwashing detergent composition useful for manual cleaning operations. Suitable components of a liquid dishwashing detergent composition shall now be discussed in greater detail.

Diamines - As noted above, diamines may be used herein in detergent compositions in combination with detergents at levels which are effective for achieving at least a directional improvement in cleaning performance. In the context of a hand dishwashing composition, such "usage levels" can vary depending not only on the type and severity of the soils and stains, but also on the wash water temperature, the volume of wash water and the length of time the dishware is contacted with the wash water.

Since the habits and practices of the users of detergent compositions show considerable variation, the composition will preferably contain at least about 0.1%, more preferably at least about 0.2%, even more preferably, at least about 0.25%, even more preferably still, at least about 0.5% by weight of said composition of diamine. The composition will also preferably contain no more than about 15%, more preferably no more than about 10%, even more preferably, no more than about 6%, even more preferably, no more than about 5%, even more preferably still, no more than about 1.5% by weight of said composition of diamine.

In one of its several aspects, this invention provides a means for enhancing the removal of greasy/oily soils by combining the specific diamines of this invention with surfactants.



Greasy/oily "everyday" soils are a mixture of triglycerides, lipids, complex polysaccharides, fatty acids, inorganic salts and proteinaceous matter.

Thus diamines, in combination with amphoteric and anionic surfactants in the specific ratios discussed below, offer the benefit of improved grease and tough food cleaning which allows the elimination or reduction in the amount of divalent ions in the preferred embodiments of the present formula. This improved cleaning is a result of diamines' proclivity as a buffering agent to increase the alkalinity of the dishwashing composition. The superior rate of dissolution achieved by divalent ion elimination even allows the formulator to make hand dishwashing detergents, especially compact formulations, at even significantly higher viscosities (e.g., 1,000 centipoise or higher) than conventional formulations while maintaining excellent dissolution and cleaning performance. This has significant potential advantages for making compact products with a higher viscosity while maintaining acceptable dissolution. By "compact" or "Ultra" is meant detergent formulations with reduced levels of water compared to conventional liquid detergents. For "compact" or "Ultra" formulations, the level of water is less than 50%, preferably less than 30% by weight of the liquid dishwashing detergent compositions. Said concentrated products provide advantages to the consumer, who has a product which can be used in lower amounts and to the producer, who has lower shipping costs. For compositions which are not meant to be concentrated, a suitable water level is less than about 85 %, more preferably less than about 70 % by weight of the liquid dishwashing detergent compositions.

Preferred organic diamines are those in which pK1 and pK2 are in the range of about 8.0 to about 11.5, preferably in the range of about 8.4 to about 11, even more preferably from about 8.6 to about 10.75. Preferred materials for performance and supply considerations are 1,3-bis(methylamine)-cyclohexane (pKa=10 to 10.5), 1,3 propane diamine (pK1=10.5; pK2=8.8), 1,6 hexane diamine (pK1=11; pK2=10), 1,3 pentane diamine (Dytek EP) (pK1=10.5; pK2=8.9), 2-methyl 1,5 pentane diamine (Dytek A) (pK1=11.2; pK2=10.0). Other preferred materials are the primary/primary diamines with alkylene spacers ranging from C4 to C8. In general, it is believed that primary diamines are preferred over secondary and tertiary diamines.

Definition of pK1 and pK2 - As used herein, "pKa1" and "pKa2" are quantities of a type collectively known to those skilled in the art as "pKa" pKa is used herein in the same manner as is commonly known to people skilled in the art of chemistry. Values referenced herein can be obtained from literature, such as from "Critical Stability Constants: Volume 2, Amines" by Smith and Martel, Plenum Press, NY and London, 1975. Additional information on pKa's can be

obtained from relevant company literature, such as information supplied by Dupont, a supplier of diamines.

As a working definition herein, the pKa of the diamines is specified in an all-aqueous solution at 25°C and for an ionic strength between 0.1 to 0.5 M. The pKa is an equilibrium constant which can change with temperature and ionic strength; thus, values reported in the literature are sometimes not in agreement depending on the measurement method and conditions.

Further discussion of the pK1 and pK2 values and diamines as well as examples of preferred diamines can be found in the copending provisional patent application of Joanna M. Clarke entitled "Diols and Polymeric Glycols for Improved Dishwashing Detergent Compositions", having P & G Case No. 7408P and application serial no. 60/119,044, incorporated above.

Anionic Surfactants - The anionic surfactants useful in the present invention are preferably selected from the group consisting of linear alkylbenzene sulfonate, alpha olefin sulfonate, paraffin sulfonates, alkyl ester sulfonates, alkyl sulfates, alkyl alkoxy sulfate, alkyl sulfonates, alkyl alkoxy carboxylate, alkyl alkoxylated sulfates, sarcosinates, taurinates, and mixtures thereof. An effective amount, typically from about 0.5% to about 90%, preferably about 5% to about 50%, more preferably from about 10 to about 30%, by weight of anionic detergent surfactant can be used in the present invention.

Suitable examples of anionic surfactants may be found in the PCT application of Chandrika Kasturi et al., entitled "Liquid Detergent Compositions Comprising Polymeric Suds Enhancers", having publication number PCT WO9927058A1, published June 3, 1999, which is incorporated above. Further examples of suitable anionic surfactants are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23. Suitable anionic surfactants may further be found in U.S. Pat. No. 5,415,814 issued 16 May 1995, to Ofosu-Asante et al., all of which are hereby incorporated by reference.

Amphoteric surfactants - The amphoteric surfactants useful in the present invention are preferably selected from amine oxide surfactants. Amine oxides are semi-polar surfactants and include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected

from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Further amphoteric surfactants, and amine oxides in particular, are disclosed in the copending provisional application of Joanna M. Clarke entitled "Diols and Polymeric Glycols for Improved Dishwashing Detergent Compositions", having P & G Case No. 7408P and application serial no. 60/119,044, which is hereby incorporated in its entirety, by reference. Particular suitable for use herein, because they are low-foaming, it may be desirable to use long chain amine oxide surfactants which are more fully described in U.S. Pat. Nos. 4,316,824 (Pancheri), 5,075,501 and 5,071,594, incorporated herein by reference.

Preferably the amphoteric surfactant is present in the composition in an effective amount, more preferably from about 0.1% to about 20%, even more preferably about 0.1% to about 15%, even more preferably still from about 0.5% to about 10%, by weight.

Secondary Surfactants - Secondary deterative surfactant can be selected from the group consisting of nonionics, cationics, ampholytics, zwitterionics, and mixtures thereof. By selecting the type and amount of deterative surfactant, along with other adjunct ingredients disclosed herein, the present detergent compositions can be formulated to be used in the context of laundry cleaning or in other different cleaning applications, particularly including dishwashing. The particular surfactants used can therefore vary widely depending upon the particular end-use envisioned. Suitable secondary surfactants are described in detail in the copending provisional patent application of Chandrika Kasturi et al., entitled "Liquid Detergent Compositions Comprising Polymeric Suds Enhancers", having publication number PCT WO9927058A1, published June 3, 1999, which is incorporated above.

Solvents - A variety of water-miscible liquids such as lower alkanols, diols, polyols, ethers, amines and polymeric glycols which comprise ethylene oxide (EO) and propylene oxide (PO) groups and the like may be used in the present invention. Particularly preferred are the C1-C4 alkanols, diols and the above mentioned polymeric glycols.

When present the composition will preferably contain at least about 0.01%, more preferably at least about 0.5%, even more preferably still, at least about 1% by weight of the composition of solvent. The composition will also preferably contain no more than about 20%, more preferably no more than about 10%, even more preferably, no more than about 8% by weight of the composition of solvent.

Further examples of suitable solvents as well as their concentrations for use in a LDL compositions are disclosed in the copending provisional application of Joanna M. Clarke entitled "Diols and Polymeric Glycols for Improved Dishwashing Detergent Compositions", having P & G Case No. 7408P and application serial no. 60/119,044, incorporated above and in the copending provisional patent application of Chandrika Kasturi et al., entitled "Liquid Detergent Compositions Comprising Polymeric Suds Enhancers", having publication number PCT WO9927058A1, published June 3, 1999, which is incorporated above.

Buffering Agents—Dishwashing compositions of the invention will be subjected to acidic stresses created by food soils when put to use, i.e., diluted and applied to soiled dishes. The compositions of the present invention will preferably have a pH of at least about 8.5, preferably at least about 10, more preferably, at least about 10.5; the compositions of the present invention will also have a pH of no more than about 12, preferably no more than about 11.5, more preferably no more than about 10.9. Because the detergent compositions of the present invention are largely alkaline, the detergent compositions will contain a buffering agent capable of providing a generally more alkaline pH in the composition and in dilute solutions. Dishwashing compositions of the present invention will thus contain from about 0.5% to 15%, preferably from about 1% to 12%, most preferably from about 2% to 10%, by weight, of a buffering agent. The pKa value of this buffering agent should be about 0.5 to 1.0 pH units below the desired pH value of the composition (determined as described above). Preferably, the pKa of the buffering agent should be from about 7 to about 12. Under these conditions the buffering agent most effectively controls the pH while using the least amount thereof.

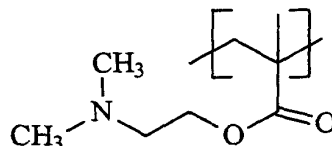
Preferred inorganic buffers/alkalinity sources include the alkali metal carbonates, alkali metal hydroxides and alkali metal phosphates, e.g., sodium carbonate, sodium hydroxide, sodium polyphosphate.

The buffering agent may be an active detergent in its own right, or it may be a low molecular weight, organic or inorganic material that is used in this composition solely for maintaining an alkaline pH. Preferred buffering agents for compositions of this invention are nitrogen-containing materials. Further examples of suitable buffering agents may be found in the copending provisional application of Joanna M. Clarke entitled "Diols and Polymeric Glycols for Improved Dishwashing Detergent Compositions", having P & G Case No. 7408P and application serial no. 60/119,044, incorporated above.

#### OPTIONAL DETERGENT INGREDIENTS:

Polymeric Suds Stabilizer - The compositions of the present invention may optionally contain a polymeric suds stabilizer. These polymeric suds stabilizers provide extended suds volume and suds duration without sacrificing the grease cutting ability of the liquid detergent compositions.

One preferred polymeric suds stabilizer is (N,N-dimethylamino)alkyl acrylate esters, namely



When present in the compositions, the polymeric suds booster may be present in the composition from about 0.01% to about 15%, preferably from about 0.05% to about 10%, more preferably from about 0.1% to about 5%, by weight. PCT application of Chandrika Kasturi et al., entitled "Liquid Detergent Compositions Comprising Polymeric Suds Enhancers", having publication number PCT WO9927058A1, published June 3, 1999, which is incorporated above.

Builder - The compositions according to the present invention may further comprise a builder system. Because builders such as citric acid and citrates impair the stability of enzymes in LDL compositions, it is desirable to include reduce the amounts or completely remove the builder salts normally utilized in LDL compositions incorporating propylene glycol as a builder. When a detergent composition includes propylene glycol solvent as a part or a whole of the detergent's carrier, enzymes are more stable and smaller amounts or no builder salts are needed.

If it is desirable to use a builder, then any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylene-diamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylene-phosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Further discussion of suitable builders can be found in the copending provisional patent application of Joanna M. Clarke entitled "Diols and Polymeric Glycols for Improved Dishwashing Detergent Compositions", having P & G Case No. 7408P and application serial no. 60/119,044, incorporated above.

If detergency builder salts are included, they will be included in amounts of from

0.5 % to 50 % by weight of the composition preferably from 5% to 30% and most usually from 5% to 25% by weight.

Enzymes - Detergent compositions of the present invention may further comprise one or more enzymes which provide cleaning performance benefits. Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, lipases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipoxxygenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases or mixtures thereof. A preferred combination is a detergent composition having a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase. Enzymes when present in the compositions, at from about 0.0001% to about 5% of active enzyme by weight of the detergent composition. Preferred proteolytic enzymes, then, are selected from the group consisting of Alcalase<sup>®</sup> (Novo Industri A/S), BPN', Protease A and Protease B (Genencor), and mixtures thereof. Protease B is most preferred. Preferred amylase enzymes include TERMAMYL<sup>®</sup>, DURAMYL<sup>®</sup> and the amylase enzymes those described in WO 9418314 to Genencor International and WO 9402597 to Novo.

Further non-limiting examples of suitable and preferred enzymes are disclosed in the copending provisional patent application of Joanna M. Clarke entitled "Diols and Polymeric Glycols for Improved Dishwashing Detergent Compositions", having P & G Case No. 7408P and application serial no. 60/119,044, incorporated above.

Because hydrogen peroxide and builders such as citric acid and citrates impair the stability of enzymes in LDL compositions, it is desirable to reduce or eliminate the levels of these compounds in compositions which contain enzymes. Hydrogen peroxide is often found as an impurity in surfactants and surfactant pastes. As such, the preferred level of hydrogen peroxide in the amine oxide or surfactant paste of amine oxide is 0-40 ppm, more preferably 0-15 ppm. Amine impurities in amine oxide and betaines, if present, should be minimized to the levels referred above for hydrogen peroxide and preferably should be less than 1 ppm.

#### Magnesium ions

While it is preferred that divalent ions be omitted from LDL compositions prepared according to the present invention, alternate embodiments of the present invention may include magnesium ions.

It is often desirable to exclude all divalent ions from the present LDL compositions, because such ions may lead to slower dissolution as well as poor rinsing, and poor low temperature stability properties. Moreover, formulating such divalent ion-containing

compositions in alkaline pH matrices may be difficult due to the incompatibility of the divalent ions, particularly magnesium, with hydroxide ions.

Nonetheless, the presence of magnesium ions offers several benefits. Notably, the inclusion of such divalent ions improves the cleaning of greasy soils for various LDL compositions, in particular compositions containing alkyl ethoxy carboxylates and/or polyhydroxy fatty acid amide. This is especially true when the compositions are used in softened water that contains few divalent ions.

But in the present invention, these benefits can be obtained without the inclusion of divalent ions. In particular, improved grease cleaning can be achieved without divalent ions by the inclusion of organic diamines in combination with amphoteric and anionic surfactants in the specific ratios discussed above while enzymes have been shown to improve the skin mildness performance of the present LDL compositions.

If they are to be included in an alternate embodiment of the present LDL compositions, then the magnesium ions are present at an active level of from about 0.01 % to 1 %, preferably from about 0.015 % to 0.5 %, more preferably from about 0.025 % to 0.1 %, by weight. The amount of magnesium ions present in compositions of the invention will be also dependent upon the amount of total surfactant present therein, including the amount of alkyl ethoxy carboxylates and polyhydroxy fatty acid amide.

Preferably, the magnesium ions are added as a hydroxide, chloride, acetate, sulfate, formate, oxide or nitrate salt to the compositions of the present invention. Because during storage, the stability of these compositions becomes poor due to the formation of hydroxide precipitates in the presence of compositions containing moderate concentrations of hydroxide ions, it may be necessary to add certain chelating agents. Suitable chelating agents are discussed further below and in U.S. Pat. No. 5,739,092, issued April 14, 1998, to Ofosu-asante, incorporated herein by reference.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetrates, N-hydroxyethylethylenediaminetriacetates, nitrilo-tri-acetates, ethylenediamine tetraproprionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldi-glycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder. Similarly, the so called "weak" builders such as citrate can also be used as chelating agents.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

#### Other Perfumes

In addition to the perfume and fragrance materials mentioned above, the present detergent compositions may also include various other natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Further examples of perfume ingredients useful herein can be found in the copending provisional patent application: "Dishwashing Detergent Compositions Containing Organic Diamines for Improved Grease Cleaning, Sudsing, Low temperature stability and Dissolution", having P & G Case No. 7167P, application serial no. 60/087,693, incorporated above. It should be noted that these additional ingredients which come under the heading "Other Perfumes" are included in addition to the perfume composition formulations discussed above.



Other Ingredients - The detergent compositions will further preferably comprise one or more deterative adjuncts selected from the following: soil release polymers, polymeric dispersants, polysaccharides, abrasives, bactericides and other antimicrobials, tarnish inhibitors, builders, enzymes, dyes, buffers, antifungal or mildew control agents, insect repellents, perfumes, hydrotropes, thickeners, processing aids, suds boosters, brighteners, anti-corrosive aids, stabilizers antioxidants and chelants. A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, antioxidants, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C<sub>10</sub>-C<sub>16</sub> alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C<sub>10</sub>-C<sub>14</sub> monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous.

An antioxidant can be optionally added to the detergent compositions of the present invention. They can be any conventional antioxidant used in detergent compositions, such as 2,6-di-tert-butyl-4-methylphenol (BHT), carbamate, ascorbate, thiosulfate, monoethanolamine(MEA), diethanolamine, triethanolamine, etc. It is preferred that the antioxidant, when present, be present in the composition from about 0.001% to about 5% by weight.

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C<sub>13-15</sub> ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach

catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Further, these hand dishwashing detergent embodiments preferably further comprises a hydrotrope. Suitable hydrotropes include sodium, potassium, ammonium or water-soluble substituted ammonium salts of toluene sulfonic acid, naphthalene sulfonic acid, cumene sulfonic acid, xylene sulfonic acid.

#### Non-Aqueous Liquid Detergents

The manufacture of liquid detergent compositions which comprise a non-aqueous carrier medium can be prepared according to the disclosures of U.S. Patents 4,753,570; 4,767,558; 4,772,413; 4,889,652; 4,892,673; GB-A-2,158,838; GB-A-2,195,125; GB-A-2,195,649; U.S. 4,988,462; U.S. 5,266,233; EP-A-225,654 (6/16/87); EP-A-510,762 (10/28/92); EP-A-540,089 (5/5/93); EP-A-540,090 (5/5/93); U.S. 4,615,820; EP-A-565,017 (10/13/93); EP-A-030,096 (6/10/81), incorporated herein by reference. Such compositions can contain various particulate deterative ingredients stably suspended therein. Such non-aqueous compositions thus comprise a LIQUID PHASE and, optionally but preferably, a SOLID PHASE, all as described in more detail hereinafter and in the cited references.

The compositions of this invention can be used to form aqueous washing solutions for use hand dishwashing. Generally, an effective amount of such compositions is added to water to form such aqueous cleaning or soaking solutions. The aqueous solution so formed is then contacted with the dishware, tableware, and cooking utensils.

An effective amount of the detergent compositions herein added to water to form aqueous cleaning solutions can comprise amounts sufficient to form from about 500 to 20,000 ppm of composition in aqueous solution. More preferably, from about 800 to 5,000 ppm of the detergent compositions herein will be provided in aqueous cleaning liquor.

The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

#### EXAMPLES

Table I

Light Duty Liquid dishwashing detergents of the present invention are as follows:

Suds boosting polymer <sup>1</sup>	0.2	--	0.7	--
Ethanol	6.0	7.0	8.0	5.5

Betaine	--	--	--	2
Water-soluble Cyclodextrin	0.05	0.5	1.5	2.5
Anionic Surfactant <sup>2</sup>	25	26	27	28
Protease	0.01	--	--	--
Amylase	--	0.001	--	--
Fragrance Materials	0.008	0.05	1.25	2.0
Diamine <sup>3</sup>	0.5	0.5	0.5	0.25
Nonionic <sup>5</sup>	4.0	5.0	3.0	4.0
Amine Oxide <sup>4</sup>	1.5	7	8	--
Sodium cumene sulphonate	3.5	3.5	3.5	1.75
Citrate	2.6	--	--	--
Mg <sup>2+</sup>	0.7	--	--	--
Polyethylene glycol (2700)	1.0	0.5	1.0	0.5
Water	Balance	Balance	Balance	Balance
pH @ 10 %	9	9	9	9

1: Polymer is (N,N-dimethylamino)ethyl methacrylate homopolymer

2: C12-13 alkyl ethoxy sulfonate containing an average of 0.6 ethoxy groups.

3: 1,3 bis(methylamine)-cyclohexane

4: C<sub>12</sub>-C<sub>14</sub> Amine oxide.

5: Nonionic may be either C10 Alkyl ethoxylated surfactant containing 8 ethoxy groups or C10 Alkyl ethoxylated surfactant containing 8 ethoxy groups.